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Flow and Fracture in Spinel Structured Ceramics
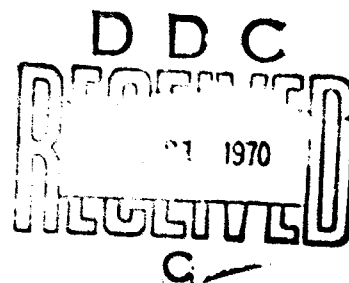
Hayne Palmour III
Chief Investigator

FINAL REPORT

FLOW AND FRACTURE IN SPINEL STRUCTURED CERAMICS

by

Hayne Palmour III

D D C

January, 1970

Department of Engineering Research
North Carolina State University at Raleigh

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INTRODUCTION

This Final Report under Contract DA 31-124-ARO-D-207, "Flow and Fracture in Spinel Structured Ceramics" describes research conducted at North Carolina State University under the direction of Dr. Hayne Palmour III, Chief Investigator, during the period from April, 1964 through August 1968. It also describes thesis research concerned with sapphire whisker reinforced spinel (initiated under this contract) which continued through mid-1969.

The Report includes sections which describe (1) the Scope of the work, (2) Scientific Personnel, (3) Publications and Technical Reports generated under the contract, or as a consequence of it, and (4) a Technical Summary of the work accomplished. In the latter, the research done under this particular contract is placed in context, both chronologically and thematically, in the overall spinel research effort which has been under way at this laboratory since mid-1960, primarily under U. S. Army sponsorship.

SCOPE

The Contractor will exert its best efforts:

    a.   To conduct theoratical and experimental high temperature studies of plasticity in spinel single crystals and of flow and subsequent fracture processes in polycrystalline spinel ceramics.

    b.   To determine the combined effects of temperature and strain rate upon the flow and fracture behavior of spinel, thus facilitating calculation of apparent activation energies and the identification of a probable rate controlling process (or processes).

    c.   To relate, whenever possible, the findings from single crystal studies to the more complex polycrystalline case, to the end that the relative roles of the crystalline grains and the less-than-crystalline grain boundaries in flow and fracture processes might be better understood.

In September, 1966, the Scope was modified to include:

    d.   To determine precipitation characteristics of $CaZrO_3$ and other compounds precipitated in $MgAl_2O_4$.

    e.   To investigate the relationship of length-width aspect ratios and other shape factors of a precipitate, temperature, and strain rate to the mechanical properties of the polycrystalline spinel.

In August, 1967, the Scope was further modified to include:

    f.   To increase the high temperature strength (and possibly, the room temperature strength as well) through the incorporation of sapphire whiskers in amounts up to several volume percent as a reinforcing phase in polycrystalline spinel.

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SCIENTIFIC PERSONNEL
1964 - 1968

Faculty

Dr. Hayne Palmour III, Research Professor of Ceramic Engineering*

Graduate Students Supported Primarily Under This Contract

Dong M. Chay**
Ph. D. Degree (ceramics) awarded June, 1965

R. Douglas McBrayer
Ph. D. Degree (ceramics) awarded June, 1965

Ronnie A. Bradley
M. S. degree (ceramics) awarded August, 1968

Graduate Students Supported in Part Under This Contract

Curtis E. Zimmer (N.D.E.A. Fellow)
M. S. Thesis (ceramics) in final draft; expect to award
degree, May 1970. Ph. D. dissertation in progress

Halit Zafer Dokuzoguz
Ph.D. degree (chemistry) awarded August, 1969
(Subject unrelated to this project)

D. Ray Johnson (N.S.F trainee)
M. S. degree (ceramics) awarded January, 1968
(Subject unrelated to this project); Ph. D.
dissertation (ceramics) being drafted, outgrowth
of work initiated under this project, expect to
award degree May, 1970

Apurva R. Desai
M. S. degree (ceramics) awarded May, 1967
(Subject unrelated to this project)

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*Although my colleague, Dr. W. Wurth Kriegel, was not supported under
this particular contract, it is appropriate (1) to note that he has
continued his active interest in our spinel studies and (2) to acknowledge
his many contributions to this research effort.

**Originally Dong M. Choi; spelling changed at time of naturalization ;
U. S. citizen.

D. E. Witter (employed as undergraduate)
M. S. degree (ceramics) awarded August, 1967
(Subject related in part to this project)

M. L. Huckabee (employed as undergraduate)
M. S. thesis (ceramics) in final draft, expect to award
degree May, 1970; Ph. D dissertation in progress
(Subject unrelated to this project)

J. W. P. Smithwick III
Left school for industrial position; completion of
M. S. degree unlikely

Graduate Student Associated With, But Not Supported by This Project

Donald R. Rummler (Research Engineer, NASA, Langley)
M. S. degree (ceramics) awarded May, 1966; Ph. D.
dissertation research now underway on topic which is
outgrowth of this project

Undergraduate Laboratory Assistants

L. J. Ferrell
B. S. degree (metallurgy) awarded August, 1966;
Professional degree (metallurgy) awarded May, 1967.

R. F. Greene
B S degree (ceramics) awarded May, 1964

James Holzgraf
B. S degree (ceramics) awarded May, 1968

W. S. Huntley
B S. degree (ceramics) awarded May, 1969

PUBLICATIONS AND TECHNICAL REPORTS

1. Dong M. Choi and Hayne Palmour III, "Fractographic Evidence of Multiple Slip in Deformed Hot Pressed Spinel", Chapter 25, pp. 473-482, in W. W. Kriegel and Hayne Palmour III, Ed., University Conferences on Ceramic Science - 1964; The Role of Grain Boundaries and Surfaces in Ceramics, Materials Science Research. Vol. 3, 631 + xiv pp, Plenum Press, New York, 1966.

2. D. M. Choi, "Flow and Fracture of Hot Pressed Polycrystalline Spinel at Elevated Temperature," Unpublished Doctoral Dissertation, Department of Mineral Industries, North Carolina State University at Raleigh, 1965 [See D. M. Choi and Hayne Palmour III, Technical Report No. 2, 88 pp., Contract DA-31-124-ARO-D-207, U. S. Army Research Office, Durham, August, 1965].

3. R. D. McBrayer, "High Temperature Deformation of Alumina Rich Spinel Single Crystals in Compression," Unpublished Doctoral Dissertation, Department of Mineral Industries, North Carolina State University at Raleigh, 1965. [See R. D. McBrayer and Hayne Palmour III, Technical Report No. 3, 79 pp., Contract DA-31-124-ARO-D-207, U. S. Army Research Office, Durham, August, 1965].

4. Hayne Palmour III and D. Ray Johnson, "Phenomenological Model for Rate Controlled Sintering," pp 779-791, Sintering and Related Phenomena, G. C. Kuczynski, N. A. Hooton and C. F. Gibbon, Eds., Gordon & Breach, Publishers, New York, 1967.

5. Hayne Palmour III, "Multiple Slip Processes in Magnesium Aluminate at High Temperatures," Proc. British Ceram. Soc. (6) 209-224 (June, 1966).

6. L. D. Barnes, "Rate Controlled Hot Pressing of Magnesium Aluminate Spinel," Unpublished Master of Science Thesis, Department of Mineral Industries, North Carolina State University at Raleigh, 1967.

7. Dong M. Chay, Hayne Palmour III and W. W. Driegel, "Microstructure and Room Temperature Mechanical Properties of Hot Pressed Magnesium Aluminate as Described by Quadratic Multivariable Analysis," J. Am. Ceram. Soc. 51 (1) 10-16 (1968)

8. D. R. Rummler and Hayne Palmour III, "Vacuum Hot Pressing of Magnesium Aluminate," J. Am. Ceram. Soc. (6) 320-326 (1968).

9 D. E. Witter, R. A. Bradley, D. R. Johnson and H. Palmour III, "Computers in Ceramic Research," Ceramic Age 84 (11) 28-31 (1968); Errata, ibid 85 (1) 8 (1969)

10. Hayne Palmour III, Ronnie A. Bradley and D. Ray Johnson, "A Reconsideration of Stress and Other Factors in the Kinetics of Densification," Chapter 22 (pp 392-407) in Kinetics of Reaction in Ionic Systems (T. J. Gray and V. D. Frechette, Eds.) Materials Science Research, Vol. 4, Plenum Press, New York, 1969.

11. R. A. Bradley, "The Effect of Doping and Heat Treatment on the High Temperature Strength of Polycrystalline Magnesium Aluminate," Unpublished Master of Science Thesis, Department of Mineral Industries, North Carolina State University, 1968.

12. C. E. Zimmer, "Sapphire Whisker Reinforced Spinel," Master of Science Thesis Research, in progress at North Carolina State University, Raleigh, 1969.

13. Hayne Palmour III and Halit Zafer Dokuzoguz, "Finely Divided Spinel," U. S. Patent Application filed March 5, 1968; Amendment filed January, 1970

14. Hayne Palmour III, "Flow and Fracture in Spinel Structured Ceramics," in Report of the Military Theme Review on Ceramics for Structural Use, held at U. S. Army Materials and Mechanics Research Center, Watertown, Massachusetts (September, 1969) U. S. Army Research Office, Durham, February, 1970 [In press].

Flow and Fracture in Spinel Structured Ceramics

Hayne Palmour, III
Chief Investigator

INTRODUCTION

This report is concerned primarily with the most recent findings
in a continuing program of research on magnesium aluminate spinel ceramics
spanning a period of more than eight years. This research effort at
North Carolina State University has been supported primarily by the
U. S Army Research Office, Durham, under Contracts DA-01-009-ORD-903
"Slip Processes in Fine Grained Polycrystalline Spinel, $MgAl_2O_4$" and
DA-31-124-ARO-D-207 (4932-MC), "Flow and Fracture in Spinel Structured
Ceramics"

EARLY OBJECTIVES AND ACCOMPLISHMENTS
1960   1964

At the time this program was initiated, the structural performance
of spinel ceramics had been little studied. Available data on mechanical
properties of spinel were both scanty and only representative of relatively
impure, coarse grained, and incompletely densified material. Consequently,
during the first years, much of the effort was devoted to (1) syntheses
of better starting materials, at first by direct reaction of mixed oxides,
and thereafter by calcination on chemically prepared coprecipitates, and
(2) densification by hot pressing methods. High density, fine grained
spinel of 99.95+% purity was shown to have significantly improved room
temperature mechanical properties, viz., bend strength 33,000 psi compressive
strength 390,000 psi, and Young's modulus of elasticity 35 x 10^6 psi.

High temperature deformation involving plastic flow processes was
observed during densification by hot pressing, as well as in dense com-
pressive specimens tested at elevated temperatures. Above the apparent

ductile-brittle transition temperature (-1250°C), compressive strength decreased with increasing temperature High purity $MgAl_2O_4$ (coprecipitated, 99.95+% purity), when properly densified by hot pressing, was found to be much stronger at temperatures 1300°C than compacts of comparable density produced from 99 5% pure starting materials which had been prepared by direct reaction of mechanically mixed alumina and basic magnesium carbonate powders.

The ductility of polycrystalline spinel observed at temperatures above ~1250°C was entirely consistent with expectations, since, in theory, its crystallographic structure should permit a sufficient number (five) of independent slip systems to meet the Taylor-von-Mises criterion for generalized plastic deformation. The cubic close packed oxygen sublattice and the dispositions of the Mg^{++} and Al^{+++} cations give rise to multiple 111 slip planes and <110> slip vectors. In terms of the geometry (but not necessarily the mobility) of glide dislocations which can bring about plastic deformation, spinel is quite comparable to ductile face-centered metals like aluminum, copper, gold, and nickel. Hence, the property of plastic flow at elevated temperatures, though highly unlikely in many ceramic systems (most have lower crystal symmetry, and fewer independent slip systems), is entirely consistent with the constitution and structure of spinel ceramics. These initial studies on the preparation and properties of spinel have been described elsewhere.[1-5] Related studies on spinel single crystal synthesis and properties conducted within this same time period under Air Force sponsorship have also been reported [6-9]

RATE CONTROLLED DENSIFICATION CONCEPTS
1963 - 1969

Concern with densification processes for spinel at both practical and conceptual levels lead to the development of novel laboratory methods for rate controlled densification and thereafter, to phenomenological kinetic models which treat densification as a modified creep deformation process. Initially worked out for hot pressing, the rate control concept has broadened to cover both simple and stress augmented sintering. [2, 4, 10, 11-13]

The most recent in the series of papers describing these densification concepts   presents a quite general phenomenological model for densification which includes the combined contributions of surface and applied forces and of annealable excess internal energy (if applicable).

Benefits to technology (and possibly to science) which might derive from these "dividend" studies of densification kinetics under rate control may well rank highest among the accomplishments of this whole body of research Certainly, these benefits will be large in proportion to the level of effort actually invested in this pertinent, but essentially peripheral, activity undertaken to assure good specimens for the primary studies of strength and deformation

One more or less direct consequence of this phase of the program was the demonstration (in cooperation with Mr. Edward Carnall Jr. of Eastman Kodak Company) of the attainment of a high degree of optical transparency in small (1 inch dia) polycrystalline spinel disc.[*] High optical quality (85% transmittance) and generally favorable density, microstructure, mechanical properties and chemical durability combine to make transparent polycrystalline spinel a promising candidate material for certain structural uses, including some ballistic armor applications. Further studies in this direction have been undertaken in recent months at North Carolina State University under Contract DAAG46-69-C-0097, "Development of Polycrystalline Spinel For Transparent Armor Applications" under sponsorship of the U S. Army Materials and Mechanics Research Center, Watertown, Mass.

*All photographs and photomicrographs requiring halftone reproductions
 have been excluded from this Final Report. Interested readers are
 referred to a fully illustrated text included in the Report of a recent
 Military Theme Review

... provided experimental confirmations
... ... and of polycrystalline
... ... ive stresses at high temperatures.
... ... of high temperature
... ... for alumina rich spinel single
... ... ations. A comparable kinetic
... ... crystalline spinel spanning a
... ... (0.5 - 200 μ). [5] Additional
... ... (without loss of structural integrity)
... ... polycrystalline spinel over the
... ... briefly summarized in the following
...

... ... about 4% in compression
... ... directions at temperatures
... ... 0.001 min^{-1} and 0.1 min^{-1}
... ... dependence of plastic deformation.
... ... is entirely consistent with
... ... consideration of (111) [110]
... ... the flow stresses required
... ... decrease with increasing
...

... ... measure of the kinetics of deformation in
single ... ... based upon variations in critical
... ... function of two independent
... ... and reciprocal absolute
... ... of the form

$$\tag{1}$$

... each orientation tested,
... ... would be reciprocally
... ... coefficient, n, and apparent
... ... creep rate equation

$$\tag{2}$$

The value of n ranged from 4.5 to 1.76, decreasing with increasing temperature $(1,550^{\circ} - 1,850^{\circ}C)$ for a given orientation. It also diminished at a given temperature with increasing numbers of active slip-systems, e.g., at $1,550^{\circ}C$ the value was 4.5 for [110], 3.9 for [111] and 2.9 for [100].

Apparent activation-energies increased with increasing stress for a given orientation. For [110] and [111] the values ranged from approximately 100 kcal/mole at 500 psi to 192 kcal/mole at 3,500 psi and for [100], from 73 to 170 kcal/mole over the same stress range. On the basis of the kinetics, dislocation etch-pit studies, and microscopic observations of extensive polygonization which had occurred simultaneously with straining, McBrayer concluded that dislocation climb was a principal mechanism in recovery processes in spinel undergoing deformation.

Compression of Polycrystalline Spinel

A comparable study of high temperature deformation in poly-crystalline spinel has also been carried out relating ultimate flow stress, σ, to three independent variables, i.e., average grain size (before deformation), d, normal strain rate, $\dot{\epsilon}$, and reciprocal absolute temperature, 1/T. Choi's study was based upon hot pressed spinel of high density (>99.2% of theoretical) and high purity (>99.94%) The experimental design incorporated grain sizes ranging from 0.5 to 200 m, strain rates from 0.0005 to 0.05 min^{-1} and temperatures from $1,350^{\circ}$ to $1,800^{\circ}C$. Statistically significant quadratic (temperature variable) and interaction (grain size/temperature, strain rate/temperature) terms were reported, yielding a flow stress equation of the form

$$\sigma = k[d^{m(1-A/T)}] \quad . \quad [\dot{\epsilon}^{1/n(1-B/T)}] \quad . \quad [e^{Q/RT(1-C/T)}] \quad (3)$$

As in the earlier case, the n and Q terms carry the same significance as those in the normal strain rate/normal stress form of equation (2) The general equation would also include an additional modifying term, d^{-m} to express grain size dependence

$$\dot{\epsilon} = Kd^{-m}\sigma^n e^{-Q/RT} \quad (4)$$

in a creep-rate equation generally analogous to that proposed by Dorn. With increasing temperature, the value of m, the grain size coefficient, changes from -0.29 to +0.23, crossing zero (indicative of negligible grain size effect) at approximately $1,570^{\circ}C$. The value of n, the stress/strain coefficient, decreased from 6.7 at 1,350 to

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1.8 at 1,800°C, and the apparent activation energy, Q, increased gradually from 166 to 198 kcal/mole with increasing temperature. "   nic observations of wavy slip, polygonization, recrystallization, and grain boundary sliding occurring during deformation, together with the kinetic data, led Choi to conclude that two or more processes were participating in plasticity, with relative contributions being dependent on temperature and to a lesser extent upon grain size.

The very good agreement between Choi's and McBrayer's kinetic data for compressive deformation of polycrystalline and single-crystal spinel leads one to consider the principal deformation process in each case to be the same. It clearly does involve slip of dislocations on multiple planes, and the preponderance of evidence suggests that dislocation climb is the most significant process in recovery.

Choi and Palmour have observed multiple slip bands within individual large grains in cyclically deformed polycrystalline spinel by optical replication fractography. They attributed microstructural alterations to strain-anneal processes, and loss of strength (failure on third cycle) to the increased grain size and related work hardening effects described by the Stroh-Petch relationship.

Bending of Polycrystalline Spinel

Fig.2 of Ref. 18 shows a specimen after approximately 5% outer-fiber tensile strain, accomplished at 1,700°C at strain rates which ranged from 0.00125 $\min^{-1}$ to 0.01 $\min^{-1}$, but principally at the latter value. The flow stress at 0.01 $\min^{-1}$ was about 200 psi, with a very slight upward trend indicative of work-hardening. At the conclusion of the test, the specimen was intact, with every indication of full retention of structural integrity

Kinetics of Deformation in Bending

Plots of ln $\dot\varepsilon$ as a function of lnσ for seven such bending experiments over the range 1,450–1,700°C are shown in Fig.1 and, for comparison, some data from McBrayer's deformation of [111] oriented single crystals and from Choi's compression   polycrystalline spinel are included. All show a strong stress/strain rate dependence, with the constant n having average values near 3.

Evaluation of the data yield an empirical rate equation for bending of the form

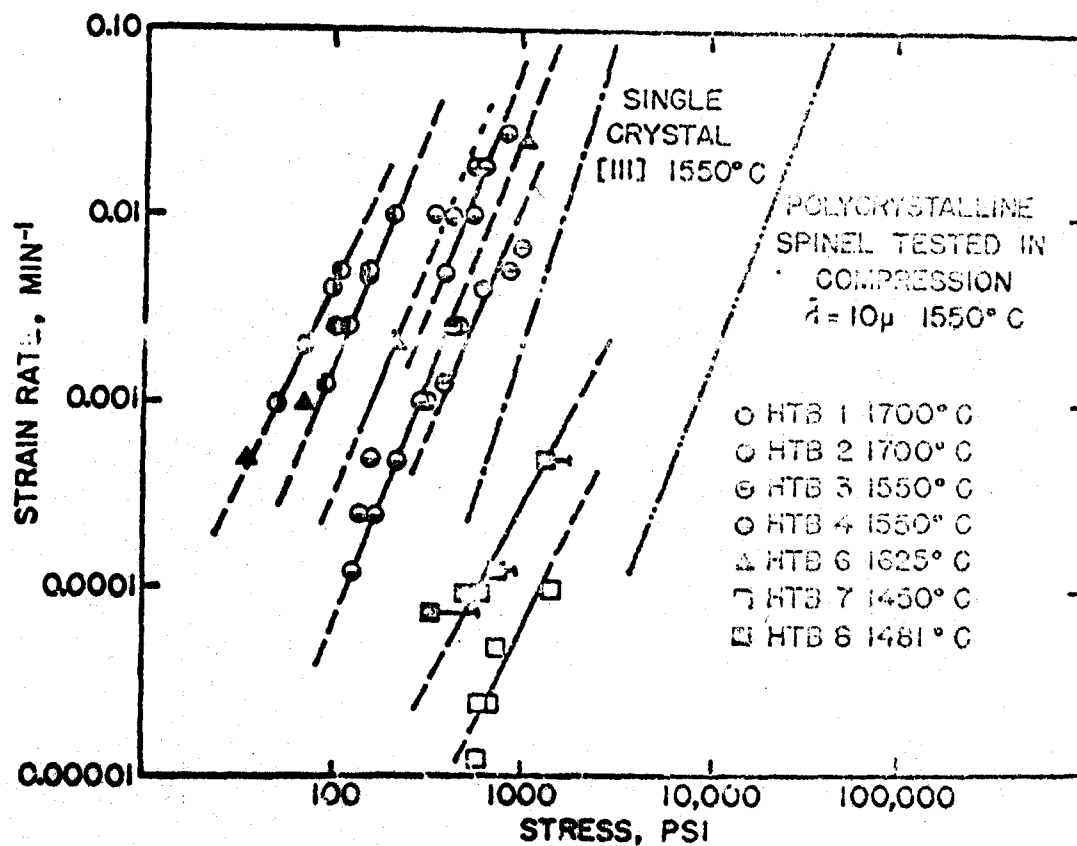$$\dot\varepsilon = \sigma^n e^{-Q/RT} \tag{5}$$

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Figure 1. Ln stress - Ln strain rate relationships for polycrystalline spinel deformed in bending at temperatures between 1450° and 1700°C.[16]

Includes comparative compression data for polycrystalline spinel[16] and alumina-rich spinel single crystals[15] tested at 1550°C.

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where, in this experiment

$$\dot{\epsilon} = 0\ 375 \times 10^{15}\ \sigma^{2.7}\ e^{-214,000/RT} \qquad (6)$$

There is a reasonably close agreement with Choi's data
(n ~2.9, Q ~182 kcal at 1,550°C).

Conclusion

   Spinel of high purity and fine grain-size is a ductile
ceramic when deformed by bending at high temperatures.
Above 1,450°C, and particularly above 1,550°C, it dis-
plays strain-rate sensitivity, strain hardening, recovery,
extensibility, and other plastic traits one normally
associates with a face-centered metal. Under favorable
conditions it is not brittle in bending unless the strain
rate is high, well in excess of 0.01 min^{-1}. However, the
onset of plasticity reduces useful strength to a relatively
low level, not because of fracture, but because of rapid
creep. This factor should be taken into account in any
engineering application of pure fine-grained spinel at
these temperatures.

   The availability of a reasonably ductile polycrystalline
ceramic at experimentally attainable temperatures does
suggest some interesting possibilities for future investi-
gation. One can predict with real certainty that spinel
will continue to be attractive as a model material for
research studies concerned with hot working and strengthening
of high-temperature materials.[8]

STRENGTHENING BY DOPING AND HEAT TREATING,
AND BY WHISKER REINFORCING
1966 - 1969

   This final phase of the investigation has come about as a logical
consequence of the findings of the preceding studies of plastic
deformation in spinel at elevated temperatures. The demonstrable
ductility of spinel under these conditions is of considerable scientific
and technological interest because of its almost metal-like behavior
in terms of retention of structural integrity during deformation.
However, like many unalloyed f.c.c. metals, pure spinel may well be
too ductile at elevated temperatures to qualify for serious condieration

in applications where deformation by creep (i.e., gradual deformation
under essentially static stress) would be unacceptable.

Therefore, two different studies were undertaken to examine possible
means of strengthening spinel to make it more resistant to deformation
at high temperatures. In one study, the effects of small concentrations
of a deliberate refractory additive, $CaZrO_3$, and of systematic heat treat-
ment subsequent to densification were investigated.[19] In the other,
sapphire single crystal whiskers (typically 3-6μ dia., with length-
diameter aspect ratios on the order of 75:1) were incorporated in amounts
up to five volume percent in a fine grained polycrystalline spinel
matrix by hot molding techniques.[20]

Doping and Heat Treating

Bradley's study of doping and heat treating in spinel[19] utilized small
concentrations of $CaZrO_3$ ($\leq 1.0\%$) introduced during chemical preparation [21]
of the fine grained spinel starting materials. Dense 2" dia. by ~1/2"
thick compacts were formed (at Eastman Kodak Company) by hot pressing
in metal dies at $1200^{\circ}C$ and ~25,000 psi. Compacts attained a density
of ~99.7% of theoretical (considered to be 3.584 g/cc) with an average
grain size of 0.1 - 0.2μ. Sulfur residues (~0.03-0.08%,
not removed during calcination) caused reddish discoloration in all
compacts. Approximately 36 specimens measuring 0.13" x 0.13" x 0.4"
(axially aligned with the original forming direction) were cut from
each compact and subsequently ground, using diamond abrasives and
accurate jigging to assure flatness and parallelism. Specimens were
heat treated for appropriate times and temperatures in high purity alumina
boats in a globar heated high alumina tube furnace in a flowing atmosphere
of 96% argon, 4% hydrogen under a pressure differential of 1.0 in. of H_2O.

One set of specimens evaluated in influence of temperature of heat

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treatment ($1250^\circ - 1500^\circ$C) on a moderately doped composition (0.046% CaZrO$_3$). The second set investigated the combined response of two independent variables, (1) dopant concentration and (2) time of heat treatment, at a constant heat treatment temperature, 1408°C.[*] Some grain growth had occurred at 1408°C (2-5 μ, depending on time), and at 1500°C the average grain size had increased to ~10μ .

All heat treated specimens, including undoped controls, were evaluated in compression at one constant test temperature (1428°C) and strain rate (0.005 min^{-1}). Testing was carried out _in vacuo_ ($\leq 3 \times 10^{-5}$ torr) under systematically reproduced conditions of cyclic preload (750-1000 psi), heating rate (~45°C min^{-1}), and equilibration of temperature and load prior to testing. Strain measurements were indirect, using the Instron crosshead micrometers, and were corrected (from calibration data) for stress-and temperature-induced machine deflections.

Tables I and II summarize the experimental results, and Figures 2 and 3 illustrate typical stress-strain curves for doped (0.046%) and heat treated specimens as functions of heat treatment temperature and time, respectively. Before heat treatment, the 0.5% offset yield strength at 1428°C was ~2000 psi, after heat treatment at 1500°C for 24 hours, it had increased to 50,000 psi. Yield strength increases as the level of dopant or the length or temperature of heat treatment increases For constant heat treatment temperature, yield strength was found to vary quadratically with respect to dopant concentration and time of heat treatment:

$$\sigma_y = -72,672 - 51,740 \log C - 10,376 (\log C)^2 + 29,865 \log t + 10,976 \log C \log t \qquad (7)$$

where:

σ_y = 0.5% offset compressive yeild strength at 1428°C, in psi

C = CaZrO$_3$ dopant concentration, in weight percent

t = time of 1408°C heat treatment, in minutes

[*] Prior high temperature solution heat treating was not employed. The temperatures required (estimated at 1700 - 1800°C) would have resulted in serious bloating as a consequence of sulfur residues, and would have caused much undesirable grain growth.

Table I. Compressive strengths at $1428^{\circ}C$ of hot pressed spinel containing 0.046% $CaZrO_3$, heat treated at various temperatures for 24 hours.[19]

Temperature of heat treatment $^{\circ}C$	Specimen number	0.5% offset yield strength psi	Maximum stress psi	Strain at maximum stress %
1250	1	2,000	28,000	23.8
	2	2,300	27,500	27.7
	Avg	2,150	27,750	25.7
1325	1	13,300	21,000	6.2
	2	15,600	28,000	6.5
	Avg.	14,500	24,500	6.3
1408	1	26,800	33,000	2.3
	2	24,900	26,000	2.0
	Avg	25,900	29,500	2.1
1500	1	51,900	52,500	2.0
	2	50,300	50,500	1.9
	Avg	51,100	51,500	1.9

Table II. Compressive strengths at $1428^{\circ}C$ of hot pressed spinel as functions of level of $CaZrO_3$ dopant and length of heat treatment at $1408^{\circ}C$. [9]

Amount of dopant wt %	Length of heat treatment min	Specimen number	0.5% offset yield strength psi	Maximum stress psi	Strain at maximum stress %
0.046	100	1	2,000	18,000	35.1
		2	1,800	19,750	36.8
		3	2,200	15,250	33.0
		Avg	2,000	17,500	35.0
0.215	316	1	18,200	22,300	6.7
		2	18,300	22,500	6.9
		3	15,000	25,100	6.2
		Avg	17,200	22,600	6.6
0.010	316	1	16,250	30,250	8.0
		2	10,000	33,500	16.5
		3	11,750	30,750	9.2
		Avg	12,700	31,500	11.2
0.046	1,000	1	21,750	37,750	2.6
		2	21,500	46,750	1.6
		3	21,550	42,500	2.2
		Avg	21,600	43,000	2.1
0.215	3,160	1	37,500	46,750	1.7
		2	42,500	47,000	1.7
		3	40,500	47,250	1.8
		Avg	40,000	47,000	1.7
0.010	3,160	1	21,250	23,750	1.3
		2	20,500	25,500	1.3
		3	20,800	24,000	1.4
		Avg	20,900	24,500	1.3
0.046	10,000	1	34,250	36,250	1.4
		2	40,000	41,500	0.8
		3	22,250	34,500	1.5
		Avg	32,200	37,400	1.2

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Figure 2. Typical compressive stress-strain curves at $1428^{\circ}C$ and 0.005 min^{-1} for hot pressed spinel containing 0.046% $CaZrO_3$ and previously heat treated at various temperatures for 24 hours.[19]
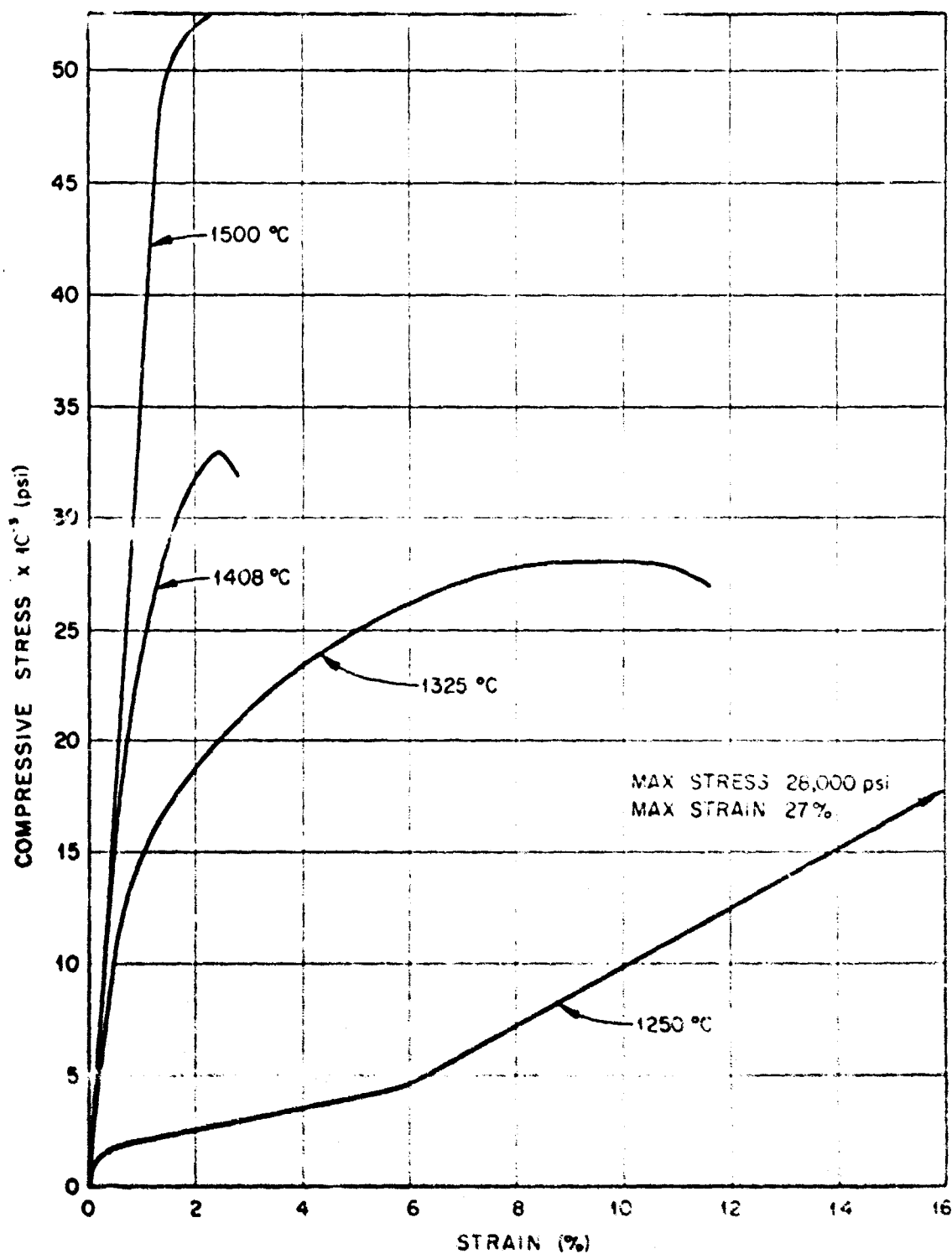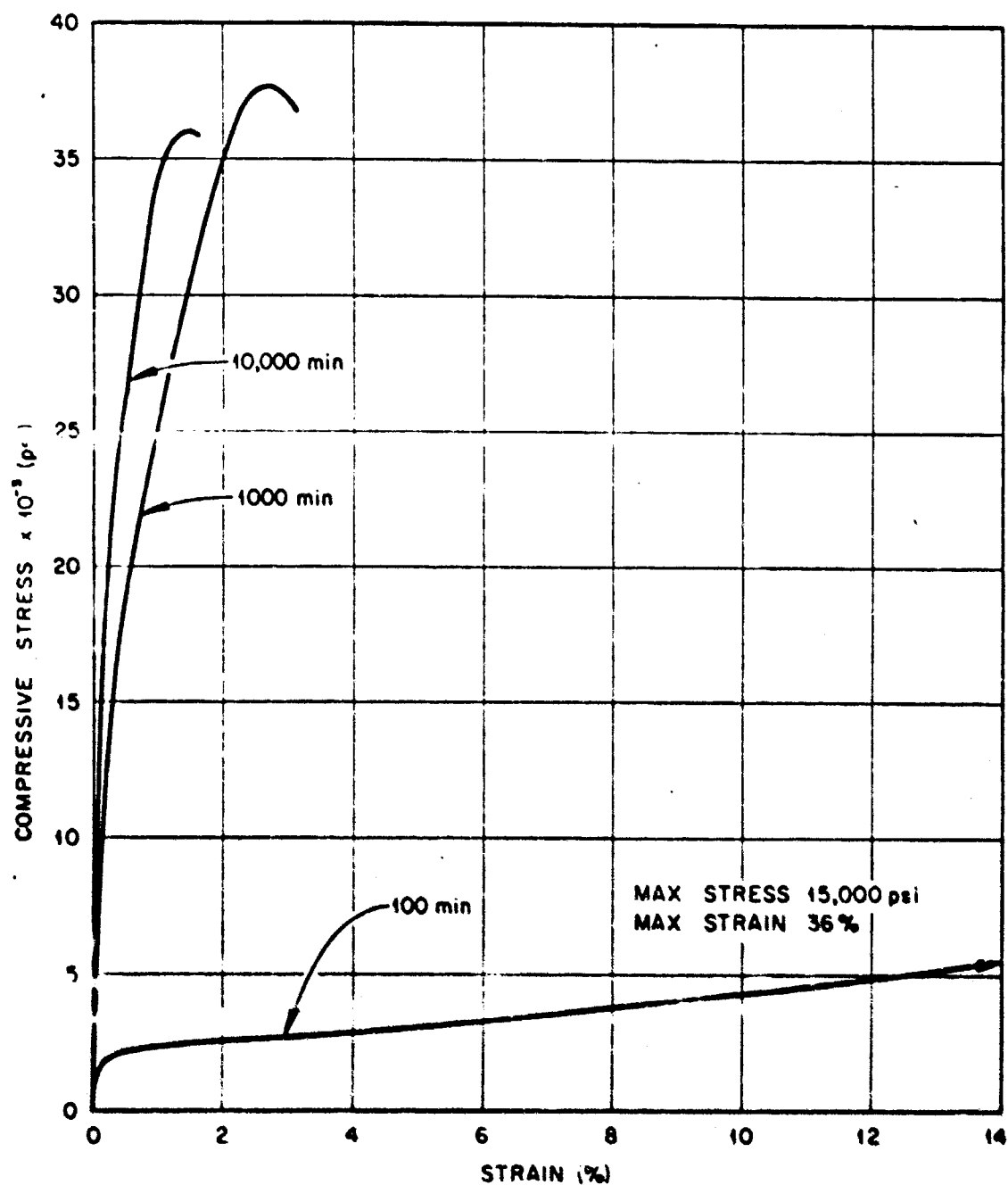
Figure 3. Typical compressive stress-strain curves at 1428°C and 0.005 min⁻¹ for hot pressed spinel containing 0.046% CaZrO₃ and previously heat treated at 1408°C for various times.[1,9]

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This regression accounted for more than 90% of all variation in the experiment; the lack of fit was found to be insignificant at the 95% level of confidence. The predicted response surface is shown in Figure 4, which illustrates both quadratic and interaction effects. At short times, the time of heat treatment is dominant, at longer times, both variables contribute to strengthening

Significant strengthening was also noted when undoped control specimens were heat treated. These findings are summarized in Table III and Figure 5.

In doped and heat treated specimens the increase in yield strength is attributed to grain growth effects coupled with a diffusion-controlled redistribution of impurities capable of providing effective retardation of dislocation movement.

Strengthening of undoped specimens as a consequence of similar heat treatment is also indicative of (a) grain size effects and (b) diffusional redistribution of uncontrolled impurities (~500 ppm). Although the yield strength of undoped, heat-treated spinel was generally comparable with similarly treated doped specimens, the total strain attained at maximum stress was appreciably higher for doped material. The larger areas beneath stress-strain curves indicated increased high temperature toughness in doped and heat treated spinel. An ultimate stress of ~51,500 psi (at 1.9% strain) was measured at $1428^{O}C$ for material doped with 0.046% $CaZrO_3$ and heat treated at $1500^{O}C$ for 24 hours.

Only limited microstructural information has been obtained to date from Bradley's deformed specimens. The mechanism(s) responsible for strengthening cannot be unambiguously identified on the basis of replication electron microscopy, and must await transmission electron microscopic studies.

Whisker Reinforcement

Zimmer's work with sapphire whisker reinforcement of a polycrystalline spinel matrix represents another alternative route to high temperature strengthening of an excessively ductile ceramic material.[20] Whiskers are tiny filamentary single crystals of exceptional perfection and strength. If they can be successfully incorporated in an appropriate matrix, stresses can be effectively coupled between the relatively weak
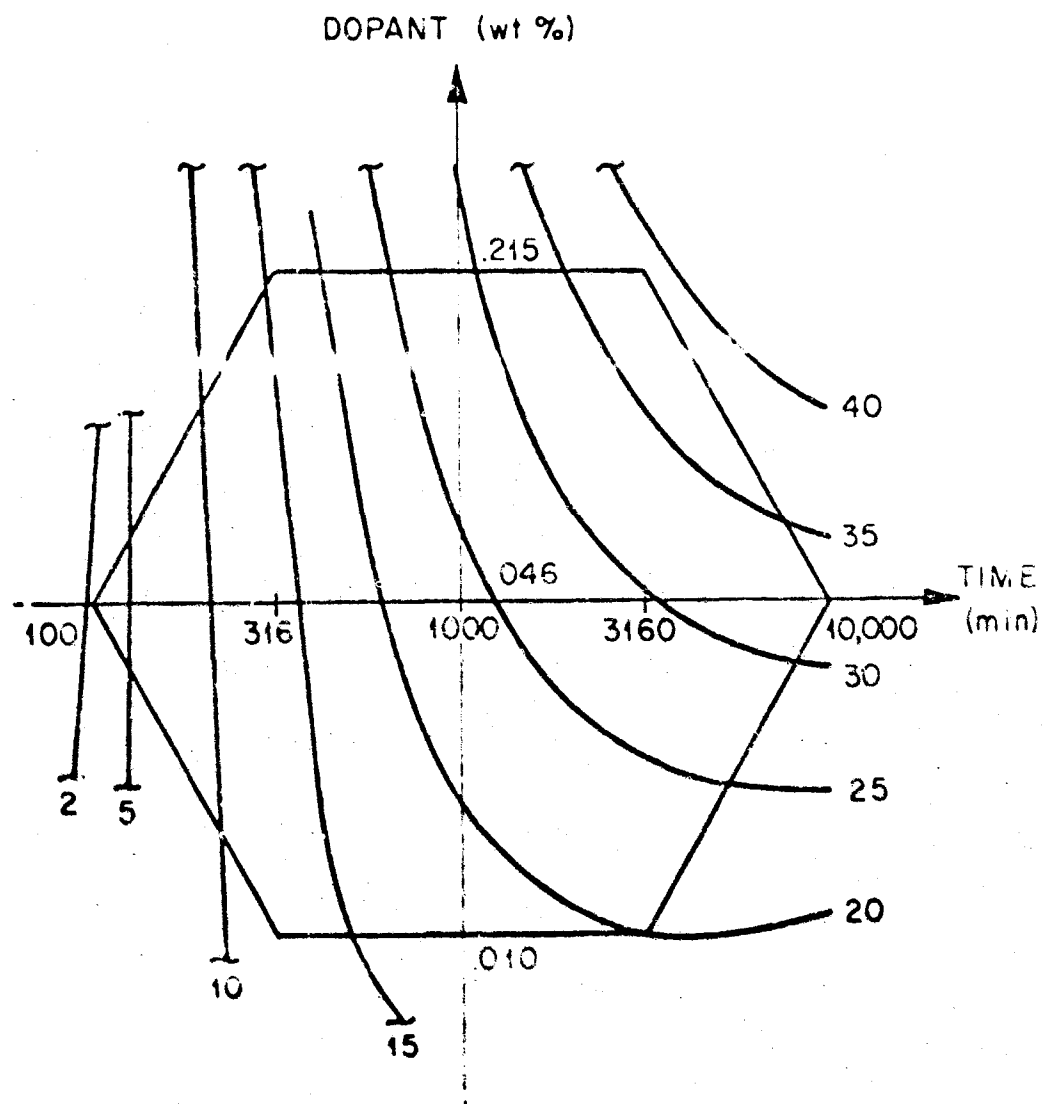
Figure 4. Contours of equal 0.5% offset yield strength [x10^{-3} psi] in compression at 1428°C and 0.005 min^{-1} for various combinations of CaZrO$_3$ dopant and time of heat treatment at 1408°C.[19]

Contours computed from Eq. 7.

Tab! III. Compressive strengths at 1428°C of hot pressed spinel,
undoped, as funtion of length of heat treatment at 1408°C.[19]

Length of heat treatment min	Specimen number	0.5% offset yield strength psi	Maximum stress psi	Strain at maximum stress %
100	1	5,000	16,750	15.0
	2	6,250	22,750	17.5
	3	5,250	29,250	26.0
	Avg	5,500	22,800	19.5
1,000	1	20,000	33,000	4.2
	2	17,500	23,500	3.9
	3	16,250	21,000	3.3
	Avg	17,900	25,800	4.2
10,000	1	34,750	38,750	0.6
	2	38,750	40,250	0.8
	3	40,250	44,250	0.6
	Avg	37,900	41,100	0.7

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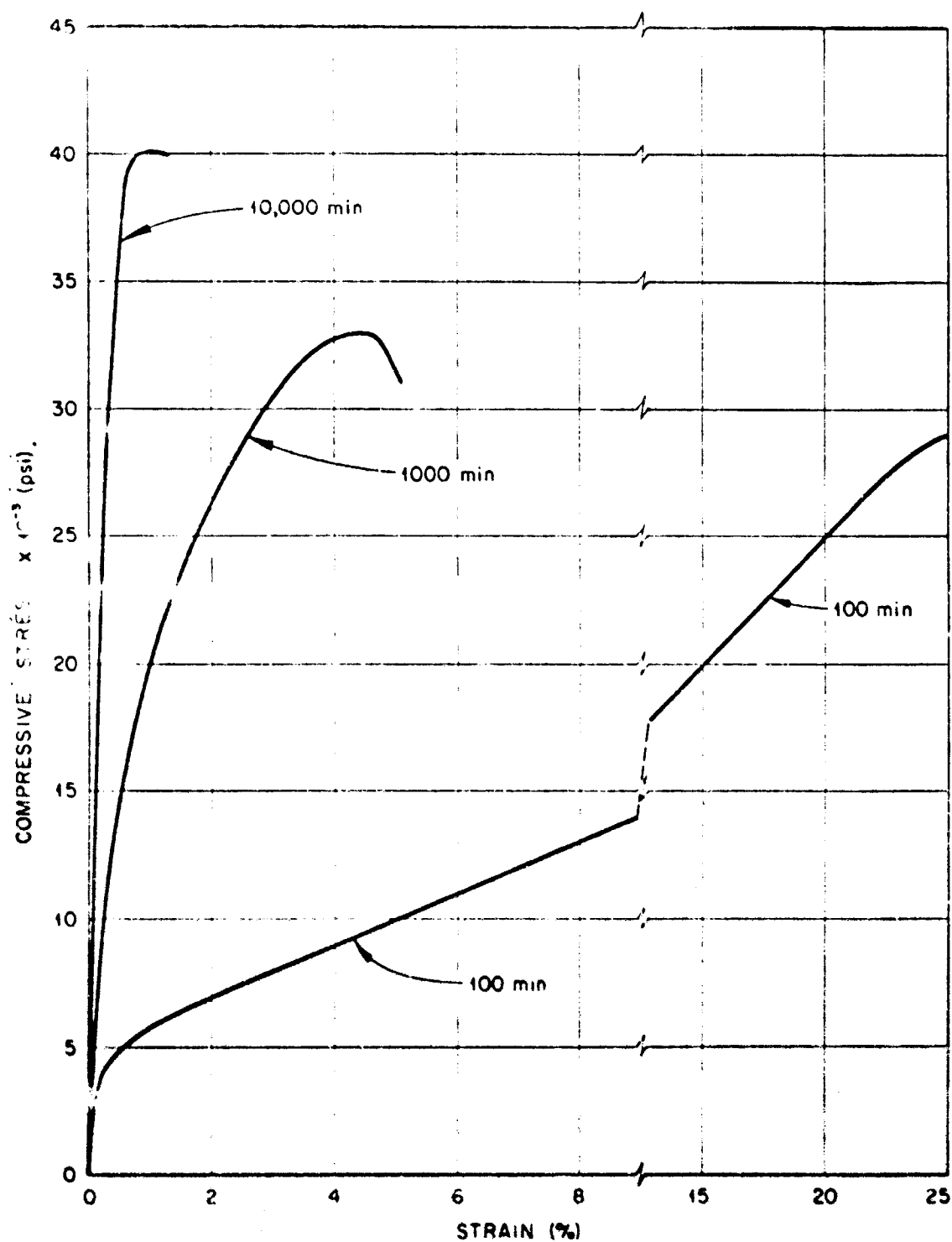COMPRESSIVE STRESS x 10⁻³ (psi).

STRAIN (%)

10,000 min

1000 min

100 min

100 min

Figure 5. Typical compressive stress-strain curves at 1428°C and 0.005 min^{-1} for hot pressed spinel, undoped, previously heat treated at 1408°C for various times. [19]

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matrix and the very strong whiskers, with resultant significant overall strength increases. Fiber reinforcement has been extensively studied in a number of composite systems with a variety of whiskers and other filaments as the reinforcing species. In general, such composites have been made of dissimilar materials: metal-ceramic, ceramic-metal, ceramic-polymer, metal-polymer, and the like. This study is rather unusual, in that it has been concerned with a strongly bonded ceramic whisker reinforced ceramic matrix.

The two phase system Al_2O_3 (whiskers) - $MgAl_2O_4$ (matrix) is not thermodynamically stable at conventional densification temperatures (>1500°C): one alumina-rich solid solution phase (involving dissolution of whiskers) would result if equilibrium were actually attained. Such a situation would be very likely in conventional hot pressing or sintering practice.

Successful incorporation of sapphire whiskers in spinel has been possible in this study as a consequence of several favorable factors. The procedures included these important aspects: (a) whiskers were intimately combined with and coated by the highly reactive spinel starting material (they were, in fact, introduced during the initial chemical process so that 300-500$\overset{o}{A}$ spinel particles were formed on them), (b) a form of rate controlled densification was employed during hot molding to achieve densification at minimum temperatures, (c) plastic deformation at about the ductile-brittle transition temperature (slightly above 1200°C) contributed significantly to the densification process during hot molding, permitting temperatures to be kept low enough to avoid excessive matrix-whisker reaction, and finally, (d) only modest temperatures were needed to achieve flow under high forming pressures (~25,000 psi) which were generated with refractory metal tooling. [It should be noted that successful densification of spinel in this fashion calls for working TZM alloy at or near its upper stress-temperature limit.]

During densification whiskers which initially had been randomly oriented became strongly oriented perpe   lar to the pressing direction; they were more or less randomly oriented within the pressing plane, and were more or less uniformly dispersed in the resultant "felt texture". Because of their low concentration, whiskers were widely separated within

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the uniform, fine grained spinel matrix (average grain size ~0.2μ).
There . no significant evide~ . of whisker degradation and the micro-
structural bond between whiskers and matrix was intimate, continuous, and
strong. As with Bradley's specimens, sulfur residues caused reddish
discoloration in all compacts. [*] Polished specimens approximately 0.1"
thick taken from the very dense 0% and 0.5% whisker compacts were optically
transparent. [Under constant hot molding conditions, compacts with
higher whisker concentrations did not attain full density, though they
closely approached it   If processing conditions were adjusted to
compensate for the higher yield stresses in material which must flow
around whiskers, it should be possible to achieve full density for
compositions containing larger volume fractions.]

Approximately 30 rectangular beam specimens measured ~0.2" x 0.1"x1.25"
were cut by diamond saw from each compact with the broad face of each
specimen being parallel to the plane of preferred whisker orientation
(molding plane). Specimens were ground flat and parallel, and then
polished (through 1/4μ diamond paste) on the tension surface prior to
testing.

Specimens were tested in four point bending in vacuo over the range
1250-1550°C, 0.0005-0.01 in/min^{-1} (beam deflection rate) using apparatus
and techniques previously described [*]

Figure 6 illustrates typical load-deflection curves as functions
of (a) deflection rate at constant whisker content and temperature and
(b) whisker concentration at constant temperature and deflection rate.
The entire experiment was characterized by extensive deformation without
loss of structural integrity. Only five of more than ninety samples
broke; one failed at 1250°C as a consequence of a visible internal flaw
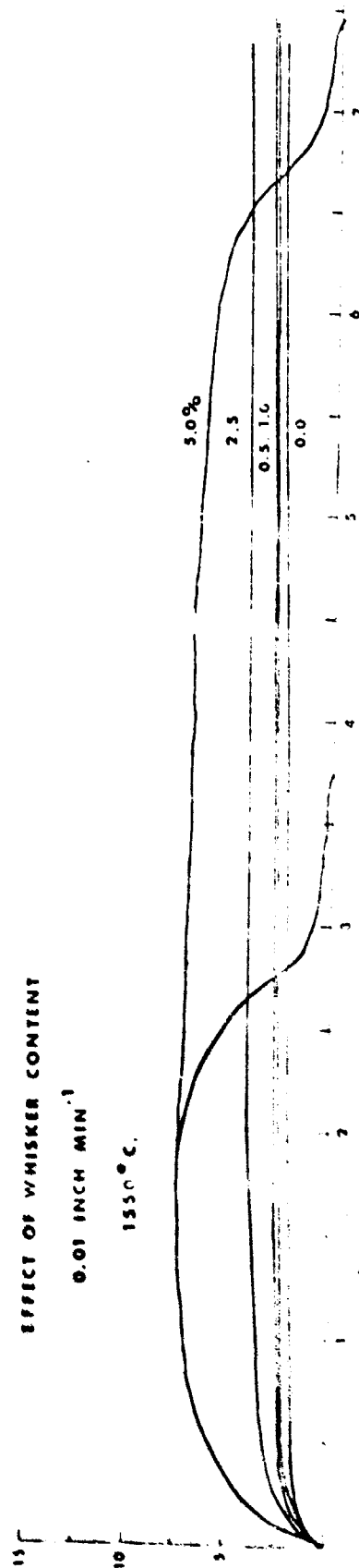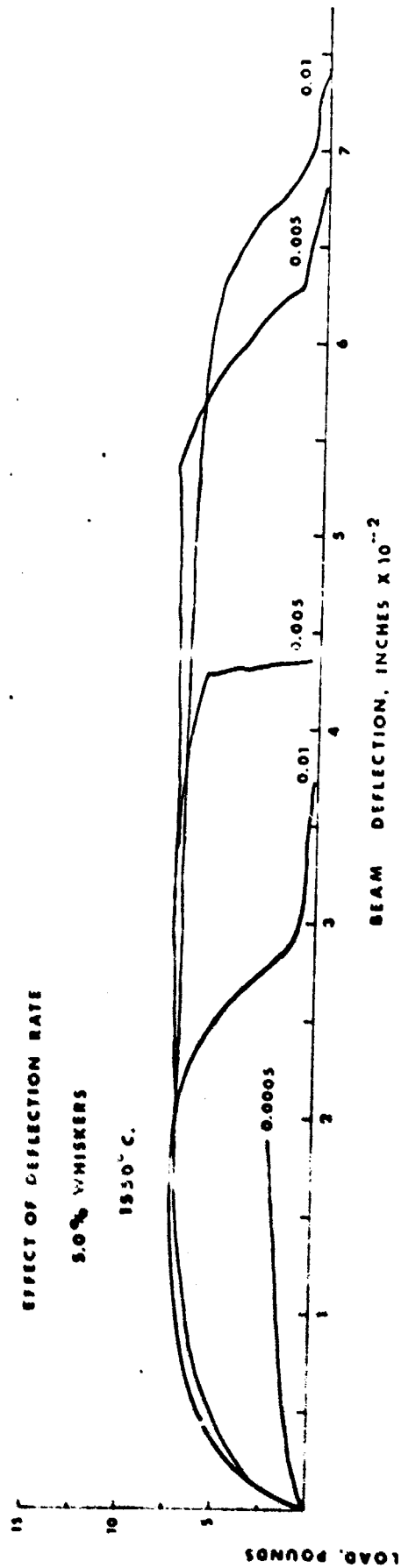near the tension surface, and two specimens containing 5% whiskers

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Figure 6. Effect of deflection rate and whisker contents, respectively, on load-deflection curves for sapphire whisker reinforced spinel tested in bending at 1550°C.[25]

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developed cracks after extensive deformation at the highest temperature
and fa⸱⸱⸱ deflection rates. As the plots show, only one failed
abruptly a. 1550°C, the others gradually lost strength as deformation
proceeded. Clearly, the whiskers were impeding crack propagation.

Statistical analyses of all data demonstrated that the results
could best be described by an equation of the form

$$\sigma_y = A \, e^{mW} \, \dot{\epsilon}^{1/n} \, e^{-Q/RT} \tag{8}$$

where:

σ_y = outer fiber yield stress at a given beam deflection, in psi

W = Concentration of reinforcing sapphire whiskers, in volume
percent

$\dot{\epsilon}$ = beam deflection rate, in inch min^{-1} (optionally, outer fiber
strain rate, in min^{-1})

T = temperature in degrees Kelvin
m, n, and Q are temperature dependent (values given in Table IV)

Regressions were computed for three separate levels of beam deflection.
Results are summarized in Table IV.

Analyses of variance indicated a very high degree of statistical
reliability for each of the overall equations. Individual
constants are reliable at the 95% level of confidence (or better).

Values for n and Q for the 0.010" and 0.025" beam deflections show
excellent agreement with each other and are nearly identical to those
reported by Choi[6] for polycrystalline spinel deformed in compression.
This agreement[6,22] is especially marked at 1550°C (a temperature
common to both studies), and is quite gratifying in view of the differences
in precursors (chlorides vs sulfates), forming techniques (graphite die
hot pressing vs metal die hot molding). deformation modes (compression vs
bending), stress criteria (ultimate strength vs flow stress at given
deflection) and even the passage of time (1964-65 vs 1968-69). The
indicated constancy of the kinetics of deformation for polycrystalline

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Table IV.   Temperature dependence of the exponents m, n, and Q (from Eq.8)
            describing the kinetics of high temperature deformation in bending
            for sapphire whisker reinforced spinel.[20]

		$1250^\circ C$	$1400^\circ C$	$1550^\circ C$
			Beam Deflection 0.001"	
m	–	0.0576	0.06352	0.16425
n		5.981	2.410	1.607
Q	–	16.44 kcal/mole	–24.95 kcal/mole	–32.05 kcal/mole
			Beam Deflection 0.010"	
m	–	0.05510	0.10476	0.23045
n		4.028	2.494	1.892
Q	–	142.36 kcal/mole	–162.45 kcal/mole	–181.40 kcal/mole
			Beam Deflection 0.025"	
m	–	0.02197	0.098990	0.20790
n		3.762	3.015	2.633
Q		–145.95 kcal/mole	–164.39 kcal/mole	–182.215 kcal/mole

Note: Choi's kinetic analysis of spinel specimens deformed in compression[16]
        showed similar temperature dependences for n and Q. At comparable
        temperatures, he reported:

	n	Q
$1428^\circ C$	4.340	172.58 kcal/mole
$1550^\circ C$	2.860	181.97

spinel (however modified) is considered to be a testimonial to true plasticitv (and its primary dependence upon crystallographic structure) at temperatures above ·1230°C Confirmation of this finding has come from microstructural evidences (not illustrated) of plastic deformation in a whisker reinforced spinel specimen deformed and finally broken at 1550°C.

MECHANICAL PROPERTIES OF POLYCRYSTALLINE SPINEL AT ROOM TEMPERATURE

Since 1964, primary research attention under this project has been directed toward high temperature strength and plasticity, but whenever possible, advantage has been taken of available opportunities to evaluate room temperature mechanical properties. In addition, some spinel specimens have been supplied to several other investigators [Anderson and Schreiber, Lamont Geological Laboratory; Pears, Southern Research Institute; Gross and Swanson, Midwest Research Institute] having special interests in (and facilities for) other pertinent property evaluations. In turn, they have made valuable data available for inclusion in this report.

Table V summarizes what are currently considered to be "best values" for a number of ambient and elevated temperature physical and mechanical properties of technological interest. One should bear in mind that all the results are subject to some compromise in terms of the adequacy of characterization of the test specimens. Stoichiometry, porosity and grain size variables were generally subject to only minor uncertainties. Cation impurities (accidental and deliberate), and especially anions, were known to be present, but their specific influence on the properties in question has not been adequately documented.

The roles of prior thermomechanical history, and of surface quality and treatment have not been ignored, but neither have they been systematically investigated, except in the limited cases represented by the work of Choi, [6] Bradley, [9] and Zimmer [?] reported here. [From many experiments, one gets the qualitative impression that spinel is probably less prone to environmental effects such as stress-corrosion (static fatigue) than either magnesia or alumina, but quantitative results are not available. One program on cyclic stress in spinel, including environmental effects, is just getting underway (D. R Rummler, NASA Langley)].

TABLE V.   CURRENT "BEST VALUES" FOR PHYSICAL AND MECHANICAL
           PROPERTIES FOR MAGNESIUM ALUMINATE SPINEL.[*]

1. Spinel Structure (Ref. 6)

    Space Group. O_h^7 - F3 dm

    Atomic Position.

         8-fold position: 8 metal ions in (a) 000, 1/4 1/4 1/4

         16-fold position: 16 metal ions in (d), 5/8 5/8 5/8;
                               5/8 7/8 7/8; 7/8 5/8 7/8; 7/8 7/8 7/8.

         32-fold position: 32 oxygen ions in (3), uuu; $u\bar{u}\bar{u}$; 1/4-u,
                               1/4-u, 1/4-u; 1/4-u, 1/4+u; uuu; 1/4+u;
                               1/4+u, 1/4+u, 1/4-u.

    With translations: + (000, 0 1/2 1/2, 1/2 0 1/2, 1/2 1/2 0).

        A center of symmetry exists at each point of the 16-fold positions.
The unit cell contains 8 formula units or molecules of $MgAl_2O_4$. The

oxygen parameter, u, equals 3/8 for the idealized structure, but is
0.387 in the actual structure.

         Lattice Constant.

    a_o = 8.0833 $\overset{o}{A}$ at 26^oC

       = 8.06 $\pm$ 0.005 $\overset{o}{A}$ for pure spinel

       + 7.93 A for limit of solid solution at 86 mol % Al_2O_3

        X-ray Diffraction. Intensities, d-spacings, and indices of diffracting
planes of spinel are given on Card No. 5-0672, X-ray Powder Data File,
American Society for Testing Materials.

        Indexing of X-ray Patterns: Rapid indexing and orientation of cubic
crystals (including spinel) is facilitated by methods and tables presented
in D. E. Witter and H. Palmour III, "PIMAX Tables For All Cubic Crystals",
Engineering School Bulletin No. 85, 70 pp., North Carolina State University,
September, 1967.

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*Reference 6 provided a rather complete tabulation (including citations of
original sources) of crystallographic and physical constants for spinel
which were available in the literature in 1962. In the interest of com-
pleteness, some of the information is repeated here, and is so referenced.

II. Physical Constants

Melting Point 2135^oC (Ref. 6)

Density   3.6 g/cc nominal Handbook
                                        value (Ref. 6)

                                 3.584 g/cc theoretical density calculated
                                        from x-ray lattice spacings
                                        (Ref. 11, 18)

Coefficient of Thermal Expansion

   25°-1350^oC 7.9×10^{-6} C^{o-1} (Ref. 6)

   25°-230^oC 7.5-7.6×10^{-6}

   230°-950^oC 8.1-8.75×10^{-6} Pure hot pressed spinel
                                        from Bradley, (Ref. 18),
                                        2 inch specimens previously
                                        heat treated at 1200^oC,
                                        measured by D. R. Johnson
                                        (unpublished).

Coefficient of Thermal Conductivity

   100^oC   1.0357

   1200^oC   0.0130 (Ref. 6)

Specific Heat

   20° 0.2

   1040^oC   0.214-0257 (Ref. 6)

Optical Properties

   Index of Refraction 1.708 Stoichiometric spinel
                                crystal (Ref 6)

   Transmittance   (0.75-5u) .75-85% Hot pressed poly-
                                        crystalline spinel
                                        containing residual
                                        sulfur (Ref. 14)

At Room Temperature:

Strength

Four Point Bending	33,400 psi (Ref. 6)	
	up to 40,400 psi *	
Tension	~23,000 psi *	
Compression	390,000 psi (Ref. 6)	

Young's Modulus of Elasticity 35×10^6 psi, static (Ref. 6)

                                      $39\ 925 \times 10^6$ psi, dynamic **

Shear Modulus 15.89×10^6 psi, dynamic **

Bulk Modulus 27.93×10^6 psi, dynamic **

Poisson's Ratio   0.2608 **

Hardness   8 on Moh's Scale (Ref. 6)

Microhardness   DPH ~1000 kg/mm^2 (Ref. 6)

Fracture Surface Energy   11,000 $ergs/cm^2$ ***

At Elevated Temperatures:

Ultimate Strength in Bending

1260°C	33,000 psi ****

Creep Rate in Bending

1160°C,	6600 psi	0.0000183 min^{-1} ****
1260°C,	6600 psi	0.000120 min^{-1}
1260°C,	13,200 psi	~.000650 min^{-1}

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*Personal Communication, C. D. Pears, Southern Research Institute, April, 1969.

**Personal Communication, Edward Schreiber, Lamont Geological Observatory, October, 1969

***Personal Communication, Gerald D. Swanson, Midwest Research Institute, September, 1969.
[Note: Specimens supplied to Pears, Schreiber, and Swanson were selected and heat treated by D. R. Rummler from undoped and doped compacts originally prepared by Bradley, Ref. 19].

****Virgil Trick, Jr., and Frank Y. Duncan, Jr., "Creep Phenomena in Magnesium Aluminate Spinels," Unpublished M.S. Thesis, Clemson University, December 1966.

measurement, four point bending

:

	1550°C
... psi	1450 psi
...500 psi	5240 psi (Ref. 20)

... strain rate:

...)	52,200 psi
...	6,220 psi
...)	2,170 psi (Ref. 16)

| ... at 1408°C, strained 19.5%) | 22,800 psi |
| ... at 1408°C, strained 0.7% | 41,000 psi |

| ... ts at 1500°C | 51,000 (Ref.19) |
| ... | |

... ngth in Compression

... specimens tested at 0.005 min^{-1}

..., ... min at 1408°C)	2,000 psi
..., 000 min at 1408°C)	21,000 psi
..., 10,000 min at 1408°C)	32,300 psi
..., ...100 min at 1408°C)	40,000 psi (Ref.19)
..., 1000 min at 1408°C)	17,000 psi

THE FUTURE FOR SPINEL

1969 - ?

It is customary for the final portions of a report to summarize
results of experiments which have been undertaken, and to draw mean-
ingful conclusions based upon findings of the subject research. It
is also appropriate to establish links with work carried on elsewhere
with which those findings either concur or conflict. It would be
entirely appropreate to follow these customs for spinel, because
favorable results and significant conclusions and maybe some conflicts
have emerged from this body of research Many have been reported
elsewhere, and others remain to be presented and published as indicated
in the List of References. Such a "Summary and Conclusions" almost
always is done in the sense of looking back. A backward look, however,
is not really as germane to the spinel case as a sensing of the
present (mid-1969) and a forecast of the near future might be. This
project's involvement with spinel has served more to catalyze present
interest and activity on the part of others than it has to reach
definitive conclusions about the nature and properties of the material
itself. The most pertinent findings, while valid within the context
of the experiments themselves, often have been subject to compromises
in terms of purity of materials, in breadth of supporting experiments,
and in the quantity of data which could be obtained systematically.

Availability of Starting Materials and Processing Technology

Of all the problems associated with doing thinly funded exploratory
research with unfamiliar (and at the time unpopular) materials, the most
difficult probably relates to obtaining adequate quantities of adequately
pure, reproducible, and well characterized starting materials with which
to work. In the beginning, one does not really know what a "good"
material must be; thereafter, one may know, but not be able to obtain
it within the limitations imposed by the existing research environment
(including fiscal and chronological factors as well as space, facilities,
and apparatus).

That sort of situation has been particularly true for spinel, since suitably pure, finely divided stocks of starting materials have not been available from commercial sources. Chemically prepared and calcined materials developed here and elsewhere on a small laboratory scale have been available to date only in quite small quantities and were at best derived from a poorly optimized, inadequately controlled, and barely contained* process capability.

It is entirely correct to consider all work to date subject to scientific criticism and/or subsequent refinement on the grounds that researchers have not been able to work with spinel material which has been sufficiently free of cation and anion impurities to permit measurements of intrinsic properties. As a consequence of the known potential for materials-related variability and added difficulties associated with obtaining reliably densified spinel ceramics in the needed quantity, size, and shape, many of the studies have been restricted in scope to what could be learned from specimens cut from a single compact, or at best, from a few compositionally different, but similarly processed compacts. In brief, for most of this decade, spinel research has gone forward, but progress has been materials-limited, and significantly so.

Within this present year, and certainly in the future, the matter of materials availability will diminish sharply as a problem in spinel research and development. Significant levels of activity under both governmental and industrial sponsorship are being directed to pilot plant scaled optimizations of processing for chemically prepared and calcined spinel materials of controlled stoichiometry, purity, and particulate properties. Multiple successes now seem imminent.

Having a high quality starting material is in itself not sufficient--one must also have command of an appropriate processing technology for forming and densification. Highly reactive spinel particulates respond fairly well to hot pressing techniques as long as densification rates

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*Safe, effective dissipation of noxious fumes (NH_4Cl, SO_3, NO_3, etc.) generated during calcination of precursor salts has represented a particularly difficult problem. Current work has shown that a countercurrent scrubber system can be used effectively for SO_3 fumes.

are not too rapid. Obviously, the plastic nature of spinel can be
employed to advantage during hot pressing. However, most investigators
have been disappointed with results obtained in conventional sintering
of spinel under isothermal conditions. Rapidly densified spinel ceramics
(hot pressed or sintered) are likely to be characterized by extensive
pore entrapment, bloating, and exaggerated grain growth.

At the present time, considerable work involving densification of
spinel is underway in government and industrial laboratories. Rate
controlled sintering of spinel is now under study in this laboratory
(under Contract DAAG 46-69-C-0097), utilizing both the present under-
standing of plasticity at elevated temperatures and the rate controlled
densification concepts initially developed under this project [?] [0-2].

It appears that rational densification technologies for spinel
are developing rapidly, replete with emergent sintering aids, grain growth
inhibitors and/or grain refinement procedures, together with non-linear
rate programming for optimum densification. At this juncture, it seems
reasonably safe to predict that essentially full density (perhaps full
transparency) ultimately can be attained through sintering without
compromise of the fine grained microstr cure which is desirable, even
mandatory, for superior performance as a structural material

The Tasks That Remain

One of the most important tasks which remain is to achieve some
significant exposure of high quality spinel to production scaled
ceramic operations. When it is possible for the material to be
intelligently handled in ten, hundred, even thousand pound quantities
under plant conditions, really meaningful information about processing
parameters, dimensional and microstructural control, and interrelationships
(and reproducibility) of several pertinent, intimately linked properties
of spinel ceramics, all much needed, will begin to come into focus.

Thermal shock resistance, impact resistance, electrical properties,
stability in various radiation fields, and many other responses of
concern in engineering applications are at best poorly known for spinel.

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The nature of the testing involved makes such data dependent not only upon funding and research momentum, but also upon the availability of rather large (but single) populations of systematically produced specimens; this need reinforces the importance of moving spinel - in quantity - from the laboratory into the pilot plant, and beyond.

To date, in comparison with the better known and closely related alumina, spinel has had the benefit of less than a third the number of years of serious research interest, and only a tiny fraction of the investment in research, development, and applications technology. Because alumina is so versatile and well established, it is not likely that spinel will ever be really competitive on a volume basis. However, the isotropic, lower density spinel does appear to offer some significantly different combinations of useful properties (e.g., transparency, high temperature plasticity) which should give it a technological advantage over alumina - and other oxide ceramics - in a variety of interesting applications, including transparent armor and other enclosures, substrates for microelectronics, and wear-and corrosion- resistant mechanical applications.

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13. ABSTRACT

This final report describes research conducted at North Carolina State University under the direction of Dr. Hayne Palmour III, during the period from April, 1964 through August 1968. It also describes thesis research concerned with sapphire whisker reinforced spinel which continued through mid-1969. The report includes sections which describe (1) the Scope of the work, (2) Scientific Personnel, (3) Publications and Technical Reports generated under the contract, or as a consequence of it, and (4) a Technical Summary of the work accomplished. In the latter, the research done under this particular contract is placed in context, both chronologically and thematically, in the overall spinel research effort which has been under way at this laboratory since mid-1960, primarily under U. S. Army sponsorship.

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